

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.646:666.32:666.36

CERAMIC TILES CONTAINING DIOPSIDE AND CLAY RAW MATERIALS FROM KHAKASSIA

A. D. Shil'tsina¹ and V. I. Vereshchagin¹Translated from *Steklo i Keramika*, No. 3, pp. 13–16, March, 2000.

A local variety of diopside rock is investigated with a view to using it in ceramic-tile mixtures. Specifics of sintering and phase formation of ceramics are determined for the combination of diopside rock and local clays from Khakassia. A diagram is developed for choosing a tile mixture composition with the required degree of sintering. Properties of various-purpose tiles of optimum compositions are described.

Diopside rocks have a positive effect on properties of ceramics: they reduce shrinkage and deformation and improve service characteristics and durability [1, 2]. However, the practice of using diopside rocks from the Baikal Region, the Far East, and Central Asia showed that the quality of the ceramics obtained and the content of the components in the mixtures are determined by the chemical and mineralogical composition and other features of the diopside and argillaceous raw materials [1, 2]. Therefore, the present paper describes a study of the composition of diopside rock from Khakassia and its effect on the sintering, phase formation, and properties of ceramics made of local Khakass clays.

The diopside rock is located conveniently for Khakass factories: in the Pistakh area, 70 km from the city of Abakan. The rock bedding is convenient for extraction: it tapers in the form of low (up to 100 m) hill outcrops, has a massive structure and a fine- and medium-grain structure (grain size from 0.1 to 5.0–6.0 mm), and is snow-white with a light blue shade. The chemical composition of the diopside rock is as follows (wt.%): 49.40 SiO₂, 0.12 Al₂O₃, 0.03 TiO₂, 0.09 Fe₂O₃, 41.51 CaO, 5.34 MgO, 0.05 Na₂O, 0.04 K₂O, 2.98 P₂O₅, and 4.58 calcination loss.

The rock has a polymineral composition. The main minerals are diopside, calcite, and apatite, and the impurity minerals are anorthite, dolomite, hydroapatite, and hydromica. The rock is classified as apatite-calcite-diopside.

The indicated minerals are identified by x-ray phase analysis (Fig. 1) and hydrate, carbonate, and phosphate minerals are additionally identified by derivatographic analysis (Fig. 2). The endothermic effect on the DTA curve at a tem-

perature of 130°C is related to removal of water adsorbed by hydromica, and the endothermic effects at temperatures of 490, 560, 650, and 860°C are related to removal of interpack hydromica water (560, 860°C) and decomposition of hydroapatite and apatite. The endothermic effects at temperatures of 790 and 820°C are caused by decomposition of magnesium and calcium carbonates.

The exothermic effect on the DTA curve at a temperature of 318°C accompanied by a weight loss of 0.41% is usually attributed to the presence of bivalent iron in the rock. Since the x-ray analysis did not detect the presence of FeO (its main maximum at 2.14 Å is absent on the x-ray pattern), it can be assumed that either FeO is present in the rock in small quantities or this effect is caused by the presence of hydromica, for example, glauconite. Glauconite manifests an exothermic effect at a temperature of 400°C [3], and it is known that the presence of impurities can reduce the temperature of transformation.

Calcite, apatite, and anorthite impurities foster the early appearance of the liquid phase, which is indicated by the endothermic effect at a temperature of 894°C.

Thus, along with the structure-forming minerals, the rock considered contains natural fluxes. Therefore, it appears likely that using this rock in ceramics will decrease the firing temperature and improve the properties of the ceramics.

Experimental verification of the effect of the diopside rock on the sintering of ceramics was performed using stripping rocks from the Izykhskii colliery and clay from the Beloyarskii deposit (Khakassia). The clays differ in their mineralogical composition, colorant-oxide content, and refractoriness. The Izykhskii clay contains more kaolin and nearly 1.5 times less iron oxide than the Beloyarskii clay.

¹ Khakass Technical Institute of Krasnoyarsk State Technical University, Abakan, Russia; Tomsk Polytechnic University, Tomsk, Russia.

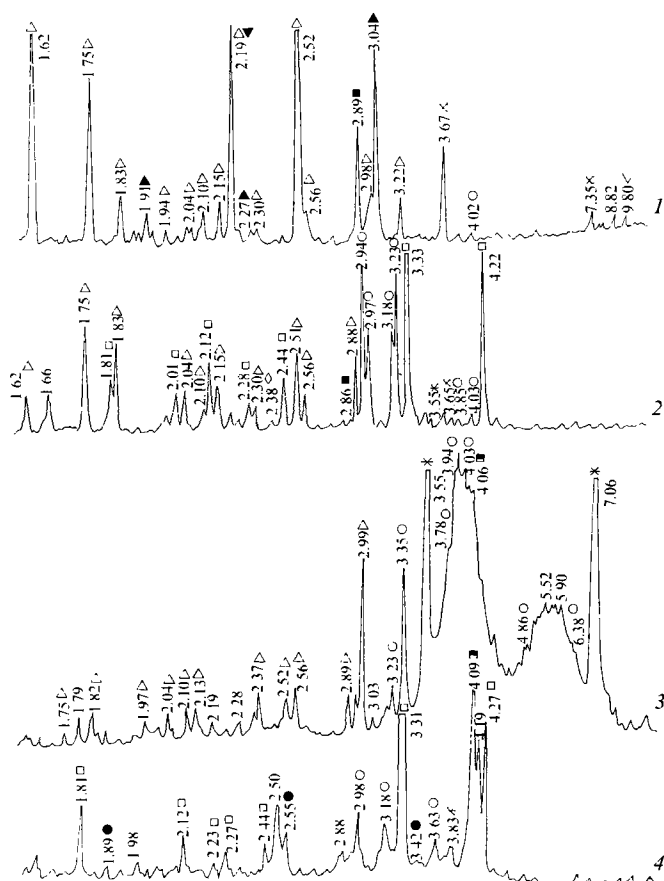


Fig. 1. X-ray patterns of the diopside rock (1), a mixture of Izykhskii clay with 45% diopside rock (2), a mixture of Izykhskii clay with 45% diopside rock and 20% cullet (3), and a mixture of Izykhskii clay with 20% cullet (4). The firing temperature of the mixtures was 1100°C; Δ) diopside; ▲) calcite; ▼) dolomite; ■) apatite; ○) anorthite; *) wollastonite; ●) mullite phase; □) quartz; ▢) cristobalite; ×) hydroapatite; v) hydromica; ◇) CaO.

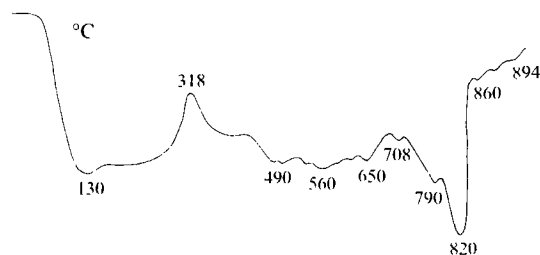


Fig. 2. DTA curve of the diopside rock.

With respect to the action of temperature, the Izykhskii clay is at the border between low-melting and high-melting clays (1310–1360°C), and the Beloyarskii clay is low-melting (1180–1200°C). Therefore, the Izykhskii clay sinters with more difficulty than the Beloyarskii clay.

The sintering of mixtures was studied on cylindrical samples 25 mm high and 25 mm in diameter. The components were milled to a residue on a sieve No. 005 of not more than 5%, the moisture content of the molding powder was

6.0–6.5%, and the sample molding pressure was 25 MPa. The molded samples were dried at a temperature of 105°C for 30 min and fired in a muffle furnace at a temperature of 1000–1100°C with an isothermal hold of 30 min.

It was found that at temperatures above 1050°C the diopside rock in an amount up to 40–45% improved the sintering of Beloyarskii clay more than that of Izykhskii clay. The water absorption of samples made of the clays mixed with 45% diopside rock is 2–3% less than the water absorption of pure-clay samples (Fig. 3). The diopside rock in an amount over 45% degrades the sintering of Izykhskii clay more than that of Beloyarskii clay. In the case of use of Izykhskii clay, the shrinkage becomes anomalous, and the size of the samples increases, although slightly. For instance, the shrinkage of samples made of 60% diopside rock and 40% Izykhskii clay is 0.6%.

In spite of some improvement in the sintering of clays with up to 40–45% diopside rock, the water absorption of samples made of binary mixtures remains high after firing at 1100°C: 9–11%.

Introduction of flux in the form of cullet for better sintering showed that the water absorption in samples made of the diopside rock and Izykhskii clay decreases significantly beginning with a 15% cullet content, and for samples containing Beloyarskii clay it starts with a 5% cullet content or more. The quantity of diopside rock and the quantity of cullet in the mixture are both significant. The change in the water absorption of samples versus the proportion of the three components in the mixtures, investigated on the example of Izykhskii clay as the plastic component, is presented in Fig. 4. Here, in the case of a cullet additive, the improved sintering of the sample with increase in the content of diopside rock in the mixture is preserved, and its positive effect on the sintering process increases up to 50%.

The sintering of ceramic mixtures with the diopside rock can be accounted for by the phase formation processes. Thus, the x-ray patterns of samples fired at 1100°C and made of binary mixtures containing 45% diopside rock (see Fig. 1) show an altered interplanar distance, a sharp decrease in the relative intensity of the apatite line (3.67 Å) from 2.0 to 0.2, and disappearance of the calcite lines, which points to their decomposition and participation in the formation of the melt and the crystalline phases. The new formations are wollastonite and calcium oxide ($d = 3.55, 2.38$ Å; $I_{rel} = 0.2$).

Presumably as a consequence of the appearance of a melt formed under the effect of apatite and calcite of the diopside rock, the sintering of binary-mixture samples improves. The calcium oxide, which partly remains in a free state, and the formation of wollastonite foster sample expansion and increased water absorption (see Fig. 3).

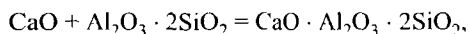
The x-ray patterns of samples fired at 1100°C and made of three-component mixtures with the same quantity of diopside rock and an additional content of 20% cullet do not exhibit lines of quartz introduced with the clay (see Fig. 1) or lines of free calcium oxide, whereas the relative intensity of anorthite and, especially, wollastonite reflections increases

sharply. The relative intensity of the line 3.55 Å, which is barely noticeable on the previous patterns, is now equal to 9.0, and the relative intensity of the new wollastonite line of 7.1 Å is 10.0 (see Fig. 1).

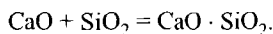
Moreover, the x-ray patterns of the fired samples of ternary mixtures exhibit an increased amount of the vitreous phase. Figure 1 shows for purposes of comparison the pattern of a sample made of clay with the same amount of cullet fired under the same conditions and but without diopside rock, and it can be seen that a higher amount of melt in ternary mixtures under firing occurs under the effect of the diopside rock, primarily, calcite and apatite, whose lines are absent on the x-ray pattern. Intensification of liquid-phase formation in firing ternary mixtures presumably fosters their improved sintering. The possibility of dissolving an additional amount of calcium oxide in the vitreous phase accounts for the expanded interval of the positive effect of the diopside rock on the sintering of ternary mixtures.

In general, the crystalline phase of the ceramics after firing at 1100°C is represented by wollastonite, anorthite, and diopside. On the one hand, this phase composition ensures low shrinkage of the samples, and on the other hand, due to anorthite crystal fusion, which is exhibited in the character of anorthite reflections with interplanar distances from 6.38 to 3.79 Å (see Fig. 1), clusters are formed with aggregation of solid particles accompanied by crack hardening. For example, the bending strength of samples made of a mixture containing 40% diopside rock is 52 MPa with a water absorption of 3.4% and a shrinkage of 3.7%.

The intensification of the processes of anorthite and wollastonite formation is probably related to the reaction between CaO, appearing on decomposition of calcite and apatite, with metakaolinite formed in clay firing and quartz introduced with clays. The reaction of CaO with metakaolinite produces anorthite



and the reaction of CaO with SiO_2 produces wollastonite



The feasibility of these reactions is supported by data obtained in studying the synthesis of anorthite from a mixture of kaolin with CaCO_3 and mixtures of CaCO_3 with Al_2O_3 and SiO_2 [4]. At a temperature of 1100°C, calcium metasilicate and anorthite were identified in the reaction mixture along with other compounds. It was noted that the reactions of formation of anorthite and intermediate compounds were intensified in the presence of mineralizers, including apatite, which is an impurity in the considered diopside rock. Moreover, crystallization of anorthite was intensified in firing of diopside-bearing porcelain mixtures [1].

Thus, the investigated diopside rock in an amount up to 40–50% (depending on the composition) improves the

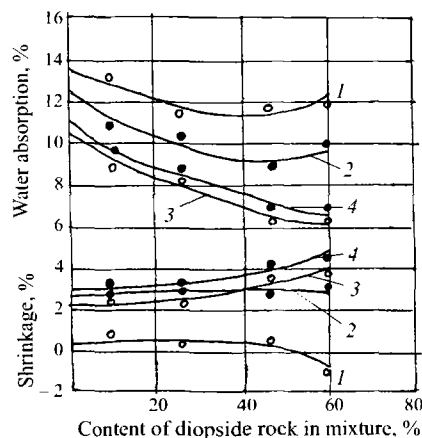


Fig. 3. Effect of the diopside rock on sintering of clays and mixtures of clays with cullet at a temperature of 1100°C: 1) Izykhskii clay; 2) Beloyarskii clay; 3) Izykhskii clay with 15% cullet additive; 4) Beloyarskii clay with 5% cullet additive.

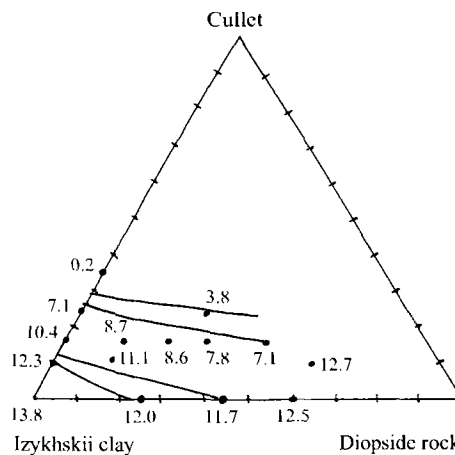


Fig. 4. Change in the water absorption of samples after firing at a temperature of 1100°C in relation to the proportion of the components in the mixture.

sintering of ceramics and fosters formation of anorthite and wollastonite, which improve the properties of ceramics.

In order to assess the properties of ceramics containing the diopside rock, tiles were made from mixtures containing it by semidry-press molding. The compositions of tile mixtures based on Izykhskii clay were selected using the diagram of water absorption versus component proportion (Fig. 4). In using Beloyarskii clay, the cullet content in the

TABLE 1

Component	Weight content, %, in composition					
	1	2	3	4	5	6
Clay:						
Izykhskii	35	—	30	—	35	—
Beloyarskii	—	52	—	43	—	45
Diopside rock	40	40	50	50	50	50
Cullet	25	8	20	7	15	5

TABLE 2

Parameter	Tiles of composition						Requirements of GOST		
	1	2	3	4	5	6	6141-91	13996-93	6787-90
Firing temperature, °C	1090	1090	1070	1070	1070	1070	—	—	—
Water absorption, %	3.4	3.2	5.7	5.3	10.4	10.1	≤ 16	≤ 9	≤ 3.5
Shrinkage, %	3.7	3.9	2.4	2.6	1.7	1.9	—	—	—
Bending strength, MPa	52	49	36	39	33	35	≥ 14	—	≥ 25
Thermal resistance, °C	130	130	130	130	130	130	125 ± 5	100	—
Moisture expansion, %	0.004	0.004	0.008	0.006	0.006	0.005	—	—	—
Cold resistance, cycles	> 50	> 50	> 50	> 50	> 50	> 50	—	≥ 35	≥ 25

mixtures was decreased to one-third. Moreover, to select the compositions of mixtures based on Beloyarskii clay, the plot of sintering of this clay with the diopside rock was used (Fig. 3). The compositions of the mixtures and the properties of the tiles are given in Tables 1 and 2.

The shrinkage of floor tiles (compositions 1 and 2) does not exceed 4%, whereas in using traditional fluxes, the shrinkage of tiles with this degree of sintering reaches 7 – 8% [5]. The shrinkage of facade tiles (compositions 3 and 4) and facing tiles (compositions 5 and 6) is within the limits of 1.6 – 2.6%. The tiles exhibit high strength (33 – 52 MPa) and cold resistance (over 50 cycles) and have a low moisture expansion (0.004 – 0.008). The facing tiles have a substantial reserve with respect to water absorption and strength, and therefore, they can be fired at a lower temperature.

The good technical parameters of the ceramics are determined by their phase composition. The crystalline phases in the ceramic matrix of the tiles are wollastonite, anorthite, and diopside.

Mixtures containing 40 and 50% diopside rock (compositions 1, 4, and 5) were tested for tile production on an automated accelerated-firing line at the Khakasstroimaterialy Ce-

ramic Tile Factory. The firing temperature for facade and facing tiles was 1070°C, floor tile 1090°C, and the firing duration was 60 min. The properties of the tiles produced on the factory line satisfy the standard requirements and support the results of the experimental studies.

Thus, use of the apatite-calcite-diopside rock in an amount of 40 – 50% in combination with local clays ensures production of high-quality tiles for various purposes.

REFERENCES

1. V. I. Vereshchagin, Yu. I. Alekseev, V. M. Pogrebenkov, et al., "Diopside rocks as a unique material for production of ceramic and other silicate materials," *VNIIESM*, Issue 2 (1991).
2. L. Z. Reznitskii, E. P. Vasil'ev, V. N. Vishnyakov, et al., "Quartz-diopside rocks of the Southern Baikal Region," *Sov. Geologiya*, No. 3, 54 – 63 (1989).
3. N. V. Logvinenko, *Petrography of Sedimentary Rocks* [in Russian], Vysshaya Shkola, Moscow (1967).
4. P. P. Budnikov and A. M. Ginstling, *Reactions in Solid-Component Mixtures* [in Russian], Stroiizdat, Moscow (1971).
5. *Chemical Engineering of Ceramics and Refractories* [in Russian], Nedra, Moscow (1986).